High Resolution Pulsed Field Ionization Photoelectron Study of O_2: Predissociation Lifetimes and High-n Rydberg Lifetimes Converging to $O_2^+(B^2\Sigma_g^-, v^+=0$ and 5)

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INTRODUCTION

The rotationally resolved photoelectron bands for $O_2^+(B^2\Sigma_g^-, v^+=0$ and 5) in the energy range of 20.27-20.95 eV have been measured using synchrotron based pulsed field ionization photoelectron techniques at an instrumental resolution of 5 cm^{-1} (full-width-at-half-maximum). In addition to the determination of accurate ionization energies and rotational constants, we have also obtained the predissociative lifetimes of 0.9 ± 0.3 ps for $O_2^+(B^2\Sigma_g^-, v^+=0)$ and 0.50 ± 0.06 ps for $O_2^+(B^2\Sigma_g^-, v^+=5)$. The (nominal) effective lifetimes for high-n Rydberg states converging to $O_2^+(B^2\Sigma_g^-, v^+=0$ and 5) are measured to be $\approx$0.4 μs, which are significantly shorter than those of $\approx$1.9 μs observed for $O_2^+(b^4\Sigma_g^-, v^+=0\text{-}5)$. The shorter (nominal) effective lifetimes for high-n Rydberg states converging to $O_2^+(B^2\Sigma_g^-, v^+=0$ and 5) are attributed to the higher kinetic energy releases (or velocities) of O^+ fragments resulting from predissociation of the $O_2^+(B^2\Sigma_g^-, v^+=0$ and 5) ion cores.

EXPERIMENT

In the supersonic beam experiment, a continuous O_2 beam was produced by supersonic expansion of pure O_2 through a stainless steel nozzle (diameter=0.127 mm, T=298 K) at a stagnation pressure of 760 Torr. As shown below, the simulation of PFI-PE spectra obtained using a supersonically cooled O_2 sample indicates that the rotational temperature of O_2 achieved is $\approx$35 K. The O_2 sample intersects the monochromatic VUV light beam 7 cm downstream in the photoionization/photoexcitation (PI/PEX) region. We have also performed PFI-PE measurements using an O_2 effusive beam, which was introduced into the PI/PEX region by a metal orifice (diameter= 0.5 mm) at room temperature and a distance of 0.5 cm from the PI/PEX region.

In the present experiment,[1] the nominal dc electrostatic field at the PI/PEX region was zero by setting the repeller plates at the same potential before the application of the Stark electric field pulse. A pulsed electric field (height=1.1V/cm, width=40 ns, delayed by 20 ns with respect to the beginning of the 60 ns synchrotron dark gap) was applied to the repeller at the PI/PEX region every one (or two, or three) ring period. The pulsed electric field was used to ionize the high-n Rydberg states and extract the PFI-PEs toward the detector. As demonstrated in the $Ne^+(^2P_{3/2})$ PFI-PE band shown in Fig. 1, the PFI-PE resolution achieved here was 0.63 ± 0.05 meV or 5.0 ± 0.4 cm^{-1} (FWHM) at 21.5648 eV.

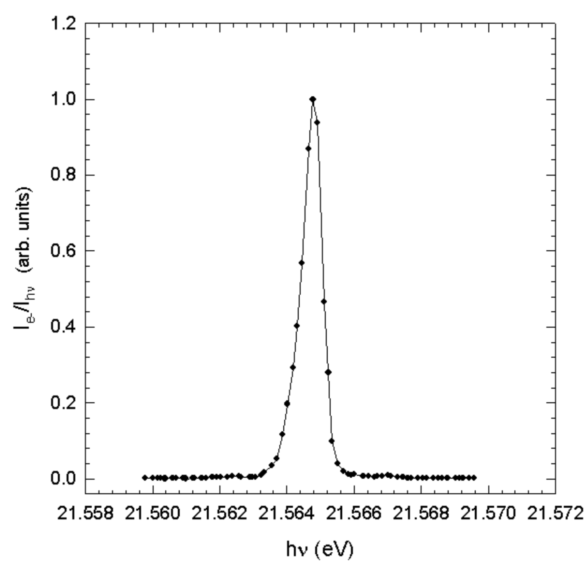

Figure 1. PFI-PE spectra of $Ne^+(^2P_{3/2})$ obtained using monochromator entrance/exit slits of 50/50 μm. The PFI-PE resolution achieved was 0.63 ± 0.05 meV.

RESULTS

Figures 2(a) and 2(b) show the PFI-PE bands for $O_2^+(B^2\Sigma_g^-, v^+=0)$ (upper curves, open circles) in the photon energy range of 20.670-20.710 eV obtained using a supersonic O_2 beam and an effusive O_2 sample, respectively. The PFI-PE band for $O_2^+(B^2\Sigma_g^-, v^+=5)$ in the energy range of 20.905-20.945 eV observed using an effusive O_2 sample is depicted in Fig. 3 (upper curve, open circles). We note that the rotational features resolved for the $v^+=0$ band are narrower than those for the $v^+=5$ band.

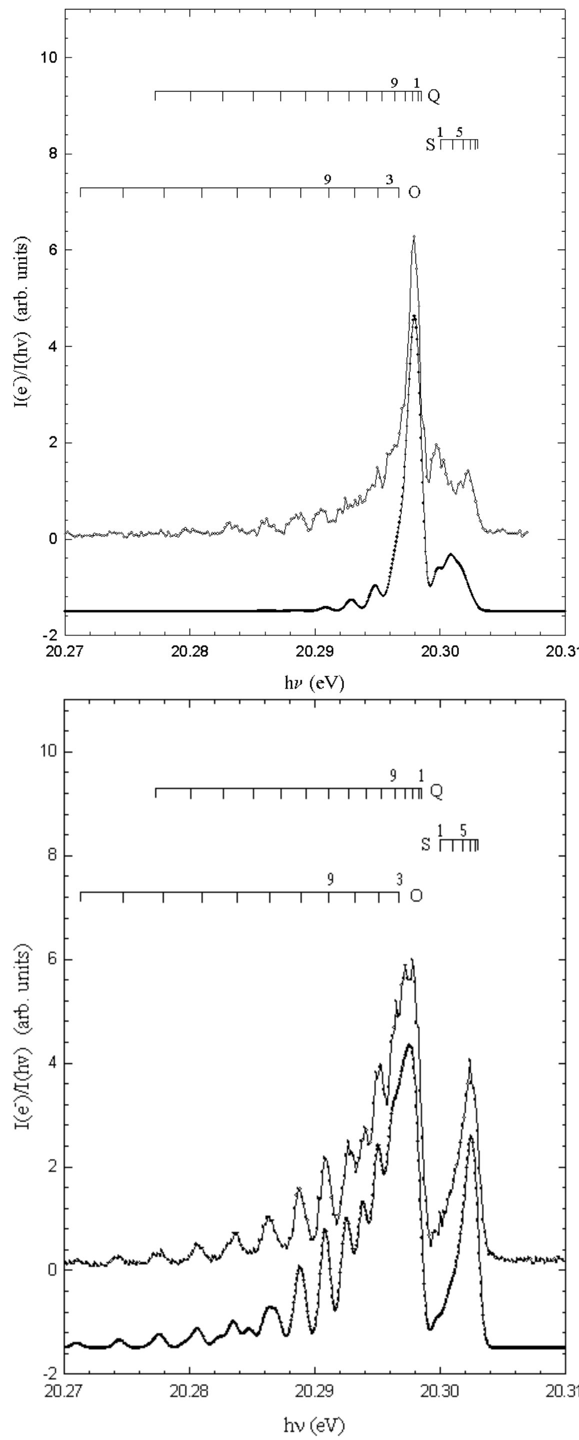

Figure 2. PFI-PE bands for $O_2^+(B^2\Sigma_g^-, v^+=0)$ (upper curves, open circles) obtained using (a) a supersonically cooled O2 sample and (b) an effusive O2 sample. The simulated spectra (lower curves, solid circles) were obtained using rotational temperatures of (a) 35 K and (b) 298 K.

The relative rotational intensities in individual vibrational bands have been simulated using the Buckingham-Orr-Sichel (BOS) model,[2] which was derived to predict rotational line strengths observed in one photon ionization of diatomic molecules. Due to nuclear spin statistics, the even levels of N" in $O_2(X^3\Pi_g)$ and N^+ in $O_2^+(B^2\Sigma_g^-)$ do not exist. Thus, only the rotational branches with ΔN (= N^+-N") = even are possible. The observed rotational branches ΔN = -2, 0, and +2 (O, Q, and S) branches, are marked in Figs 2(a), 2(b), and 3. For a g $\leftrightarrow$ g transition, the photoelectron angular momentum *l* must be odd. Thus, the partial waves for the ejected electron are restricted to the *l*=1 and 3 continuum states.

The simulation of the PFI-PE bands for v+=0 and 5 yields ionization energies (IEs) of $20.2982_5\pm0.0005$ and $20.9348_8\pm0.0005$ eV for the formation of $O_2^+(B^2\Sigma_g^-, v^+=0, N^+=1)$ and $O_2^+(B^2\Sigma_g^-, v^+=5, N^+=1)$ from $O_2(X^3\Sigma_g^-, v"=0, N"=1)$. The IEs are higher than the literature values by 2.3 and 8 meV, respectively. The simulation also yields rotational constants of 1.243±0.002 cm-1 for the v+=0 state and 1.122 ±0.002 cm-1 for the v+=5 state. These values allow the calculation of the equilibrium bond distances of re = 1.302±0.001 and 1.370±0.001 Å for the v+=0 and 5 states of O2+(B2Σg-), respectively. The latter values are greater than the r_e value of 1.2074 Å for $O_2(X^3\Sigma_g^-, v"=0)$. This observation is consistent with the fact that the formation of the $O_2^+(B^2\Sigma_g^-)$ state involves the ejection of a bonding electron from the $3\sigma_g$ orbital.

The $O_2^+(B^2\Sigma_g^-)$ state lies significantly above the first dissociation limit of $[O^+(^4S) + O(^3P)]$ at 18.73 eV and is known to be strongly predissociative. This, together with the fact that the energy of $O_2^+(B^2\Sigma_g^-)$ is more than 8 eV higher than that of the ground $O_2^+(X^2\Pi_g)$ state, makes spectroscopic and dynamical studies of $O_2^+(B^2\Sigma_g^-, v^+)$ difficult by employing the ion emission and common laser spectroscopic techniques. Although the $O_2^+(B^2\Sigma_g^-) \rightarrow O_2^+(A^2\Pi_u)$ transition is optically allowed, the emission from $O_2^+(B^2\Sigma_g^-)$ has not been observed. This suggests that the predissociative lifetimes (τ_d's) are significantly shorter than the radiative lifetimes for $O_2^+(B^2\Sigma_g^-, v^+)$. The predissociation dynamics of $O_2^+(B^2\Sigma_g^-, v^+)$ have been investigated extensively using photoelectron photoion coincidence (PEPICO) time-of-flight (TOF) techniques.[3] In these experiments, the measurement of the fragment ion TOF spectrum is triggered by the detection of a threshold photoelectron (TPE). Since the TOF of a TPE to the electron detector usually ranges from 10–100 ns, the traditional PEPICO-TOF technique is not applicable for the measurement of dissociative lifetimes shorter than 10 ns.

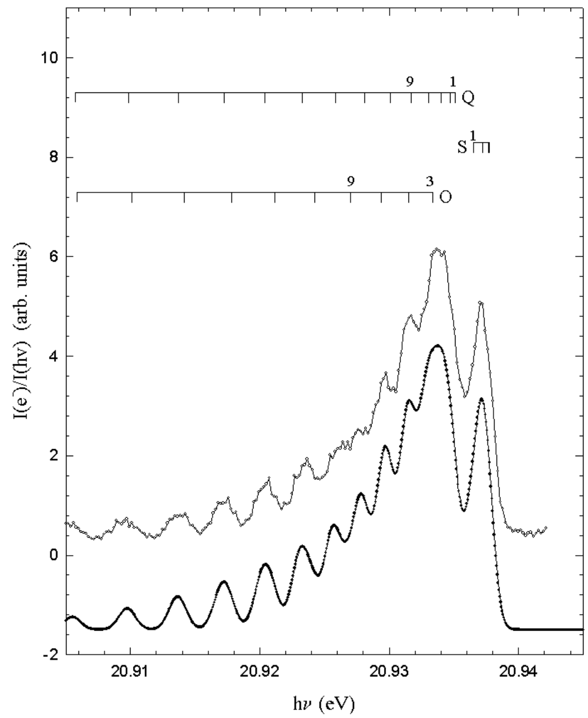

Figure 3. PFI-PE bands for $O_2^+(B^2\Sigma_g^-, v^+ = 5)$ (upper curves, open circles) obtained using an effusive O_2 sample. The simulated spectrum (lower curves, solid circles) was obtained using a rotational temperature of 298 K.

From the Gaussian linewidths used in the BOS simulation, we calculated the natural rotational linewidths for the respective v+=0 and 5 states to be 6.2±1.8 cm^{-1} and 10.9±1.3 cm^{-1}. Since the τ_d's are expected to be significantly shorter than the radiative lifetimes for $O_2^+(B^2\Sigma_g^-, v^+)$, the broadening of the rotational transitions is contributed predominantly to predissociation. Using these natural rotational linewidths we calculate the τ_d values of $(0.9\pm0.3)\times10^{-12}$ s for $O_2^+(B^2\Sigma_g^-, v^+=0)$ and $(0.50\pm0.06)\times10^{-12}$ s for $O_2^+(B^2\Sigma_g^-, v^+=5)$.

The τ values for high-n Rydberg states converging to O_2+($B^2\Sigma_u^-$, v^+=0 and 5) are measured to be ≈0.4 μs. In a similar study,4 we found that the τ values are ≈1.9 μs for high-n Rydberg states converging to the $O_2^+(b^4\Sigma_g^-, v^+=0\text{-}5)$ states, and are nearly independent of v^+. Since the $O_2^+(b^4\Sigma_g^-, v^+=4$ and 5) states are known to be predissociative with τ_d values in the range of 0.01-4 ns, it is surprising that the τ values for high-n Rydberg states converging to these unstable ion cores are found to be nearly the same as those converging to the stable $O_2^+(b^4\Sigma_g^-, v^+=0\text{-}3)$ ion cores. For an electron in a sufficiently high-n and high-*l* Rydberg state with a near circular orbital, the Rydberg electron may not respond rapidly even when the core is dissociating. This would result in a substantially longer (autoionization) lifetime for the high-n Rydberg state compared to the τd value of the ion core. The latter conclusion should be valid if the kinetic energy for the departing O^+ + O is sufficiently small. Thus, the (autoionization) lifetime of a high-n Rydberg state is effectively decoupled from the dissociative lifetime of the ion core.

Assuming that the autoionization and fluorescence lifetimes for a high-n Rydberg O_2 state, $O_2(n)$, are longer than the τ_d value of the O_2^+ ion core, a plausible decay mechanism for $O_2(n)$ is shown in reactions (1a) and (1b).

$$O_2(n) \rightarrow O(n') + O, \quad (1a)$$
$$\rightarrow O^+ + e^- + O \quad (1b)$$

If the relative velocity for the departing $O^+ + O$ fragment pair resulting from the predissociation of the O_2^+ ion core is not too high, the high-n Rydberg electron originally associated with O_2^+ in $O_2(n)$ may be guided by the Coulombic field to orbit around the departing O^+ ion forming a high-n' Rydberg O atom, O(n'). The relative velocities for the departing $O^+(^4S) + O(^3P)$ fragments from $O_2^+(B^2\Sigma_u^-, v^+=0)$ and $O_2^+(B^2\Sigma_u^-, v^+=5)$ are calculated to be 0.62×10^6 and 0.72×10^6 cm/s, respectively. The corresponding times required for O(n') fragments to move a distance of 0.15 cm, which defines the detection zone of the electron spectrometer, are 0.48 and 0.42 μs. Since these values are comparable to the τ values of ≈0.4 μs observed for high-n Rydberg states converging to $O_2^+(B^2\Sigma_u^-, v^+=0$ and 5), we conclude that the higher velocities (or kinetic energies) for O(n') formed in the dissociation reaction (1a) contribute to the short τ values for high-n Rydberg states converging to $O_2^+(B^2\Sigma_g^-, v^+=0$ and 5). The τ values presented here must be considered as nominal values.

SUMMARY

We have obtained accurate spectroscopic constants and reliable τ_d values for $O_2^+(B^2\Sigma_g^-, v^+=0$ and 5) using high resolution synchrotron based PFI-PE techniques. This method is directly applicable for τ_d measurements of other predissociative states of O_2^+ and predissociative states of other diatomic molecular ions in the inner-valence region. The results for τ measurements of $O_2^+(b^4\Sigma_g^-, B^2\Sigma_g^-)$ show that a high-n Rydberg molecular state with a predissociative molecular ion core is well defined only prior to the dissociation of the molecular ion core. Similar experiments have been performed on the $O_2^+(c^4\Sigma_u^-, v^+=0, 1)$ states and the results are soon to be published.

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REFERENCES

1. C.-W. Hsu, M. Evans. P. A. Heimann, and C. Y. Ng, Rev. Sci. Instrum., **68**, 1694 (1997).
2. A. D. Buckingham, B. J. Orr, J. M. Sichel, Phil. Trans. Roy. Soc. Lond. A **268**, 147 (1970).
3. T. Akahori, Y. Morioka, M. Watanabe, T. Hayaishi, K. Ito, and M. Nakamura, J. Phys. B **18**, 2219 (1985).
4. C.-W. Hsu, M. Evans, S. Stimson, C. Y. Ng, and P. Heimann, Chem. Phys., accepted.

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